LNT–SCR dual-layer catalysts optimized for lean NO$_x$ reduction by H$_2$ and CO

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ABSTRACT

Monolithic catalysts consisting of a layer of selective catalytic reduction (SCR) catalyst deposited on top of a lean NO$_x$ trap (LNT) catalyst were optimized to provide high NO$_x$ conversion at both low and high temperatures with minimal precious group metal (PGM) loading using H$_2$/CO reductant mixtures. The optimized dual-layer catalyst circumvents the need for urea feed and has the potential to reduce the expensive PGM loading by up to 38% from that of LNT only catalyst under laboratory test. We investigated the impact of catalyst design variables, such as SCR and LNT zoning, the ceria level in LNT, as well as SCR zeolite type (ZSM-5, SSZ-13) layer thickness. Zoning of either or both the SCR and LNT in the dual-layer catalysts enables an increase of the low-temperature NO$_x$ conversion, and minimizes the high temperature (300–400 °C) conversion loss caused by the SCR diffusion resistance and undesired NH$_3$ oxidation by the LNT. High ceria loading of the LNT enhanced NH$_3$ generation, NO$_x$ adsorption and mitigated CO poisoning at low temperatures (150–250 °C). Commercial Cu-SSZ-13 exhibited a higher NH$_3$ storage capacity and better low-temperature SCR activity than the in-house synthesized Cu-ZSM-5, and improved the low-temperature NO$_x$ conversion of the dual-layer catalysts. The diffusion resistance in the top active Cu-zeolite layer inhibited the overall NO$_x$ reduction as shown by replacing it with an inert Na-ZSM-5 layer with a high Si/Al ratio. Washcoat diffusion limitations adversely affect the high temperature performance more than the NH$_3$ oxidation to NO$_x$. The experiments revealed that diffusion limitations in the top SCR layer loading of 1.0 g/in.^{3} started at 150 °C using a pure H$_2$ feed and at 250 °C using a CO/H$_2$ feed.

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1. Introduction

The US light-duty vehicle (LDV) greenhouse gas regulations for 2017–2025 require a significant improvement in fuel economy [1]. A potential solution to this regulatory challenge is use of diesel or lean burn gasoline engines due to their higher fuel efficiency and lower CO$_2$ emissions than the stoichiometric gasoline engine. However, fuel-lean operation challenges the reduction of nitrogen oxide (NO$_x$) in a net-oxidizing atmosphere. Both the upcoming EPA Tier 3 and California's Low Emission Vehicle (LEV III) regulations require a reduction in fleet-average levels of non-methane organic gases (NMOG) + NO$_x$ by up to 81% from the current LEV or Tier 2 Bin 5 level by 2025 [2]. So far, two leading deNO$_x$ technologies have been commercialized to meet the current NO$_x$ emission standard, urea-selective catalytic reduction (urea-SCR) and NO$_x$ storage and reduction (NSR).

Urea-SCR, which involves selectively reducing NO$_x$ to N$_2$ with NH$_3$ from urea hydrolysis in the presence of excess oxygen over Cu- or Fe-exchanged zeolite catalysts, has gained widespread application for a fraction of diesel passenger cars and most heavy-duty (HD) vehicles. Urea-SCR system can achieve 90–95% deNO$_x$ efficiency, but requires an onboard urea storage and delivery system. This causes space and cost issues, especially for LD vehicles. NSR technology has potential for being applied for LD lean burn gasoline and diesel passenger cars. It involves periodic lean/rich cyclic operation over a lean NO$_x$ trap (LNT) catalyst. NO$_x$ is trapped on the catalyst under lean conditions. The trapped NO$_x$ is then reduced to N$_2$ and some undesired byproducts like NH$_3$ during a short, rich feed of a reductant mixture containing hydrocarbons, CO and H$_2$. The LNT catalyst uses expensive precious group metals (PGMs) to achieve a nominally 70–80% deNO$_x$ conversion, typically lower than that by the SCR system [2]. Active efforts are focused on increasing its efficiency while reducing the precious metal loading.

In order to meet the upcoming NO$_x$ and greenhouse gas emission standards, additional improvements are required in either the SCR or the NSR system, especially for low-temperature NO$_x$ conversion [3]. A recent, promising approach is via a combination of LNT and

SCR catalysts, which can enhance NO_x reduction while decreasing the PGM loading in the LNT catalyst and avoiding the need for urea injection to the SCR catalyst [4–8]. With the LNT + SCR technology, in situ NH_3 produced by the LNT during rich purges is captured by the SCR catalyst and used to reduce NO_x during the subsequent lean periods. Thus, the SCR catalyst improves the overall NO_x conversion of the LNT catalyst while eliminating the problematic NH_3 slip. In addition, as a fraction of NO_x is reduced by the SCR catalyst, a fraction of expensive LNT catalyst can be replaced by the much cheaper SCR catalyst. This makes the LNT + SCR system more cost-effective than either the NSR or SCR alone. Several LNT + SCR configurations were proposed, including sequential [4–7], and dual-layer configurations [8–10].

NH_3 is a key determining factor of the NO_x conversion performance of the SCR catalyst in the combined system [11]. Given that the LNT catalyst is the only NH_3 generator, it is important to understand the formation and role of the ammonia during NO_x reduction over the LNT catalyst. Pihl et al. [12] investigated product selectivity during the regeneration of the LNT catalyst by a H_2/CO reductant mixture. They reported that more NH_3 was produced either at low temperatures or high reductant/NO_x ratio. Most NH_3 was produced from NO_x stored on the slow storage sites after passage of the reductant front. Wang et al. [13] studied NH_3 formation using simulated diesel exhaust and found the NH_3 selectivity increased with steam reforming activity due to the increased generation of H_2. Clayton et al. [14] showed that NH_3 formed by the reaction of H_2 with stored NO_x would be oxidized by downstream nitrate, which was a major route for N_2 formation. They determined that favorable cyclic conditions for NH_3 generation included high H_2/NO_x ratio, moderate temperature, and low Pt dispersion [15]. Chen et al. [16] investigated the effect of the oxygen storage component (OSC) loading on NH_3 formation over LNT catalysts. They found that below 250 °C, the high OSC catalyst generated a significantly higher amount of NH_3 than the low OSC one due to the OSC promoting both the water gas shift (WGS) reaction and NO_x reduction at low temperatures. At high temperatures the opposite trend was observed.

In a sequential brick configuration, ammonia is produced in the upstream LNT during the rich feed and stored on the downstream SCR catalyst. During the ensuing lean phase the stored NH_3 reduces the NO_x that slips past the LNT via a NH_3-SCR pathway. Daimler commercialized the first LNT + SCR dual-brick aftertreatment system on the Mercedes-Benz E-Class in 2007 [17]. Chen et al. [16] proposed to optimize the dual-zone LNT–SCR system by a combination between a special LNT with enhanced NH_3 generation and an advanced SCR with excellent low temperature NH_3-SCR activity and resistance to high temperature lean/rich aging. Xu et al. [18] from Ford showed that Cu SCR catalysts are preferable to Fe SCR catalysts for the combined LNT + SCR system due to their higher low-temperature NO_x conversion and NH_3 storage capability. They also demonstrated the potential of the LNT + SCR approach to achieve LEV III with up to 30% saving in PGM loading compared to LNT alone [5].

Dual-layer LNT/SCR architecture is a potential alternative to the sequential brick configuration, in which NH_3 produced from the bottom LNT layer is captured by the SCR top layer and then utilized for additional NH_3-SCR of NO_x. Integrating SCR onto LNT via dual-layer architecture enables a downsizing of the aftertreatment system, which is desirable for applications with limited space. In addition, the intimate contact between LNT and SCR layer is expected to enhance NH_3 utilization efficiency. In contrast, with the dual-brick configuration a considerable amount of NH_3 released from the front LNT section may be oxidized by stored NO_x and oxygen in the downstream section of the LNT before it reaches the SCR brick, limiting the NH_3 supply to the SCR catalyst [4]. Morita et al. [8] from Honda first reported a dual-layer system comprising a solid acid zeolite on top of ceria-supported Pt. It was

highly efficient for low-temperature NO_x reduction to meet NO_x emission standard of Tier 2 Bin-5 [10]. They reported that the ceria-based layer functioned as an effective NH_3 generator by promoting the WGS reaction and enhancing the low-temperature NO_x storage and reduction. Recently, Honda researchers Matsuo et al. [19] further improved the dual-layer system by introducing a zirconia-based intermediate layer that minimized the negative interaction between LNT and SCR layers having opposite acid–base properties. The improved system showed rather high NO_x reduction performance even at low exhaust gas temperatures.

In addition to the adverse interaction at the interface, several inherent drawbacks are associated with dual-layer architecture. The foremost issue is the inevitable diffusional resistance by the SCR upper layer, which inhibits the effective transport of NO_x to the underlying LNT layer for storage during the lean feed and of reductants for regeneration during the rich feed. The simulation results by Koltsakis [20] showed that at either high temperature ($\geq$300 °C) or high space velocity ($\geq$50,000 h^{-1}), the dual-layer deNO$_x$ efficiency was significantly reduced by the additional resistance of the SCR layer and was lower than either the LNT alone or the dual-brick system. Another deficiency of the dual-layer is undesired oxidation of stored NH_3 to NO_x by the adjacent LNT layer at high temperatures. Trapped NH_3 in the SCR top layer can diffuse to the adjacent LNT layer and be oxidized to NO_x, especially at high temperatures. In such cases, trapped NH_3 generates additional NO_x instead of reducing the NO_x. Pihl et al. [12] reported that over a commercial LNT catalyst, the selectivity of NH_3 oxidation toward NO increased as the temperature ramped up. Liu et al. [21,22] found that adding ceria to LNT catalyst further intensified NH_3 oxidation and thus decreased the high-temperature performance of dual-layer LNT–SCR catalysts. Therefore, such detrimental effects may counterbalance or even outweigh the benefit of adding SCR layer.

We focus in this study on developing novel zoned designs of LNT–SCR dual-layer catalysts to maximize the low-temperature NO_x reduction while minimizing high-temperature conversion decline. Specifically, we investigate the impact of ceria level in the LNT for NH_3 formation, the thickness and zeolite type (ZSM-5, SSZ-13) of the SCR top layer, and of SCR and LNT zoning on cycle-averaged NO_x conversion and product selectivities. This information enables minimization of the amount of expensive PGM loading in dual-layer LNT–SCR catalysts that lead to high deNO$_x$ conversion (>80%), especially at low temperatures (<250 °C).

2. Experimental

2.1. Catalyst preparation

Monolithic LNT and SCR (Cu-SSZ-13) bricks were supplied by BASF Catalysts (Iselin, NJ). The LNT samples had a cell density of 400 cpsi and washcoat loading of 4.6 g/in.^{3}, corresponding to 60–80 μm in thickness. Cylindrical cores (D = 2.54 cm, L = 7.6 cm) were drilled out of the monolithic brick from which small monolithic pieces were prepared with a specific shape (D = 0.8 cm, L = 2.0 cm, 28 channels). The compositions of two LNT catalysts containing the same PGM, barium loading and varying ceria loadings are reported in Table 1. The metal-exchanged zeolites used in our study are described in Table 2. The Cu-SSZ-13 catalyst having an 8-membered ring, chabazite (CHA) crystal structure, referred as CuC,

Table 1
Composition of monolith-supported LNT catalysts.

	LNT1	LNT3
Formula	Pt/Rh/BaO/Al$_2$O$_3$	Pt/Rh/BaO/CeO$_2$/Al$_2$O$_3$
PGM (g/ft^3)	90	90
BaO (wt%)	14	14
CeO$_2$ (wt%)	0	34

Table 2
Composition of metal-exchanged zeolites.

	Metal (wt%)	Si/Al ratio
Cu-CHA	2.5 est.	20–30
Cu-ZSM-5	ca. 2	23
Na-ZSM-5	0.2 est.	280

was synthesized and characterized according to a patent of BASF [23]. The washcoat loading was estimated to be about 2.4 g/in.^{3} with ca. 2.5 wt% Cu loading. The in-house synthesized Cu-ZSM-5 catalyst powder with Si/Al ratio of 23, denoted as CuZ, was synthesized via a wet-ion exchange method described elsewhere [24]. Its Cu content was about 2 wt% determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

Both commercial and in-house made LNT–SCR dual-layer monolithic catalysts were used. The in-house made dual-layer catalysts used CuZ as the SCR catalyst on top of a commercial LNT3 monolith. Briefly, an aqueous Cu-ZSM5 slurry was prepared and washcoated onto the LNT3 monolith by a dip-coating technique described elsewhere [9]. Washcoating was repeated until the desired loading was obtained. The final step involved calcinations of the monolithic catalyst at 500 °C for 5 h to get a dual-layer catalyst. After washcoating, a uniform layer of CuZ (thickness of ca. 40 μm for 0.9 g/in.^{3}) was deposited on top of the LNT3 layer [9]. We referred to this dual-layer catalyst as CuZ(Y)-L(X). The "Y" is the top-layer washcoat loading of the CuZ, while the "X" indicates the bottom-layer loading of LNT3 denoted by "L". The other LNT3–SCR dual-layer monolithic catalysts, provided by BASF Catalysts (Iselin, NJ), comprised of LNT3 as the bottom layer and Cu-exchanged chabazite (CuC) as the top layer, and is referred to as CuC(Y)-L(X), using the same notation principle as above. A series of CuC-L dual-layer catalysts with varying LNT3 (1.15, 2.3, 3.45, 4.6 g/in.^{3}) and SCR (0.8, 1.6 g/in.^{3}) loadings were prepared for our study. Catalyst notation and configurations used in our experiment are reported in Table 3.

In order to investigate the top-layer washcoat diffusion resistance, an inert Na-ZSM-5 (NaZ) with a high Si/Al ratio was deposited on the LNT3 monolith instead of Cu-zeolite to form, NaZ(Y)-L(X), dual-layer catalysts. The synthesis of Na-ZSM-5 is similar to Cu-ZSM-5 except for the final ion-exchange with copper ion [24]. The as-prepared Na-ZSM-5 powder was washcoated onto the blank cordierite or LNT3 monoliths for testing. The high Si/Al ratio was used to minimize the adsorptive or catalytic properties of the zeolite catalyst.

2.2. Reactor tests

The bench-scale reactor set-up was the same as that used in our previous studies [21,25]. It comprised a gas supply, a reactor, an analytical and a data acquisition systems. Water was fed by a syringe pump (ISCO Model 500D) and vaporized in a heated line. The reactor gaseous effluents of NO, NO_2, N_2O, NH_3, CO, CO_2 and H_2O were measured by a FT-IR spectrometer (Thermo-Nicolet, Nexus 470). A quadrupole mass spectroscopy (QMS; Cirrus LM99, MKS Inc.) monitored the concentrations of H_2 and O_2 if needed. In the presence of CO, having the same m/e of 28 as N_2, the cycle-averaged formed N_2 was determined by closing an overall nitrogen balance.

A typical 60 s-lean and 5 s-rich cycle was used for cyclic operation. The fixed lean/rich cycling times simplifies the study of the impact of different catalyst design variables. The carrier gas contained 2.5% H_2O and 2.0% CO_2 in Ar. The lean feed contained 500 ppm NO and 5% O_2 in the carrier gas mixture. The rich feed contained 2.5% reductant but no NO and O_2 in the same carrier gas. Two types of reductant feeds were used: 2.5% H_2 for simulating ideal rich condition and 1.5% H_2/1.0% CO. The cycle-average H_2/NO feed ratio was 1.04 times the stoichiometric ratio needed for NH_3 formation by the reaction to promote the effective NH_3 production but minimize reductant slip: $16H_2 + 4NO + 3O_2 \leftrightarrow 4NH_3 + 10 H_2O$. The real rich exhaust is a complex mixture of HC/CO/H_2 with a CO:H_2 ratio of about 3:1. A similar study but using simulated diesel exhaust has been conducted and will be reported in another paper. Before measurements, each catalyst was exposed to 5% O_2 in Ar continuously at 500 °C for 30 min and then to above lean/rich cycling condition at 500 °C for another 30 min, using 2.5% H_2 as reductant.

The total flow rate was 1000 sccm. Unless specifically stated, the GHSV was 60,000 h^{-1} (based on total monolith volume, 2 cm long). In some cases, shorter length pieces of LNT1 and LNT3 were used to construct spatial profiles. The feed temperature was increased from 150 to 400 °C in steps of 50 °C. The time needed to reach a cyclic state in the study varies with temperature, reductant feed, the nature and loading of the catalysts. It usually takes 10 cycles for CuC/L and 5 cycles for CuZ/L at low temperatures and 3–4 cycles at high temperatures for both dual-layer catalysts. At each temperature the final ten cycles were averaged after a cyclic state was reached to determine the cycle-averaged NO_x conversion, product selectivity and NH_3 yield for a particular operating condition.
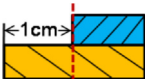
The fractional NO_x conversion was calculated by

$$X_{NO_x} = 1 - \frac{\int_0^{\tau_T} [F_{NO}(t) + F_{NO_2}(t)]dt}{\int_0^{\tau_l} F_{NO}^i(t)dt} \qquad (1)$$

The fractional NH_3 yield was calculated by

$$Y_{NH_3} = \frac{\int_0^{\tau_T} F_{NH_3}(t)dt}{\int_0^{\tau_l} F_{NO}^i(t)dt} \qquad (2)$$

Table 3
Configuration and notation of zoned and layered catalysts.

Catalysts	Configurations	LNT3, g/in.^{3}	CuC^a, g/in.^{3}
L(X)		X	–
CuC^a(Y)/L(X)		X	Y
L(X$_1$) + CuC^a(Y)/L(X$_2$)		X$_1$/X$_2$	Y

^{a} CuC may be also CuZ or NaZ in study.
CuC, CuZ, NaZ represent Cu-CHA, Cu-ZSM-5, Na-ZSM-5, respectively.

Here τ_l and τ_T are the duration of lean phase feed and a lean-rich total cycle (s). $F_{NO}^i(t)$ is the NO feed rate and $F_{NO}(t)$, $F_{NO_2}(t)$, $F_{NH_3}(t)$, are the corresponding effluent molar flow rates (mol/s).

Steady state experiments were conducted to evaluate the SCR catalyst properties. The standard SCR reaction was used to assess the activity of the CuZ, CuC and NaZ, all of which had a ~2.4 g/in.[3] loading. The feed contained 500 ppm NO, 500 ppm NH$_3$, and 5% O$_2$ in carrier gas. For the NH$_3$ storage experiments, 500 ppm NH$_3$ in carrier gas was fed to catalysts at 150 °C for 30 min until they were saturated. After then the NH$_3$ feed was shut off and the catalysts were purged by a carrier gas for another 30 min at 150 °C. The total NH$_3$ uptake was calculated by subtracting the effluent amount from that fed.

3. Results and discussion

3.1. Desired ceria level in LNT for dual-layer application

An optimal dual-layer LNT–SCR catalyst should have a high low-temperature deNO$_x$ efficiency to meet upcoming strict regulations. A higher contribution of SCR toward overall NO$_x$ conversion at low temperatures enables increased reduction of PGM loading on the LNT catalyst. To develop highly efficient LNT–SCR dual-layer catalyst at low temperatures (≤250 °C), the LNT catalyst needs to promote both NO$_x$ adsorption and NH$_3$ formation. Ceria, an effective oxygen storage component, is typically incorporated into LNT catalysts to improve their overall activity, durability and desulfation properties [26]. The impact of ceria on NH$_3$ formation during the regeneration of LNT catalysts is quite complex. It is widely accepted that NH$_3$ is produced only when the catalyst is under a net reducing condition [11,14]. Oxygen stored on ceria consumes reductants to lower the reductant/NO$_x$ ratio and delays the time at which the catalyst reaches a net reducing state. Both effects inhibit NH$_3$ formation, especially at high temperatures, as shown by Ren and Harold [27]. On the other hand, ceria increases NH$_3$ formation at low temperature by providing additional NO$_x$ storage sites and promoting the WGS reaction and NO$_x$ reduction [10,16]. Essentially, the ceria level in the LNT layer must be tuned to match the targeted temperature window to achieve optimum performance of dual-layer catalyst.

Fig. 1a–b compares the NO$_x$ conversion and NH$_3$ yield using ceria-free LNT1 and ceria-rich LNT3 catalysts. The addition of ceria to the LNT significantly increased NO$_x$ conversion at low temperature for either pure H$_2$ or CO/H$_2$ feed case mainly due to increased NO$_x$ storage capacity combined with enhanced NO oxidation by ceria-supported Pt. The difference in NO$_x$ conversion decreases as the temperature increases. The NO$_x$ conversion for LNT1 and LNT3 are similar above 300 °C. Effluent NH$_3$ yield from LNT3 is higher than that from LNT1 at temperatures below 250 °C. The difference is more pronounced when introducing CO into the rich feed. Ceria-supported precious metal catalysts exhibit several orders of magnitude higher rate of WGS reaction than precious metal alone [26], significantly promoting H$_2$ and NH$_3$ generation at low temperatures. Moreover, ceria mitigates the CO poisoning. On the other hand, at high temperatures almost no NH$_3$ breakthrough from LNT3 is observed while still appreciable amounts of NH$_3$ are emitted by the LNT1. This trend is consistent with previously reported results of Chen et al. [16].

Fig. 2 compares the spatially resolved NH$_3$, N$_2$ yields and NO$_x$ conversion along the LNT1 and LNT3 catalysts at 250 °C for a feed of 1% CO + 1.5% H$_2$. The spatial measurement was achieved by cutting monoliths into different length. LNT3 generates higher upstream NH$_3$ yield but slightly lower downstream NH$_3$ yield combined with significantly higher downstream N$_2$ yield than LNT1. This is due to the downstream NH$_3$ oxidation to N$_2$ by stored NO$_x$ and oxygen in
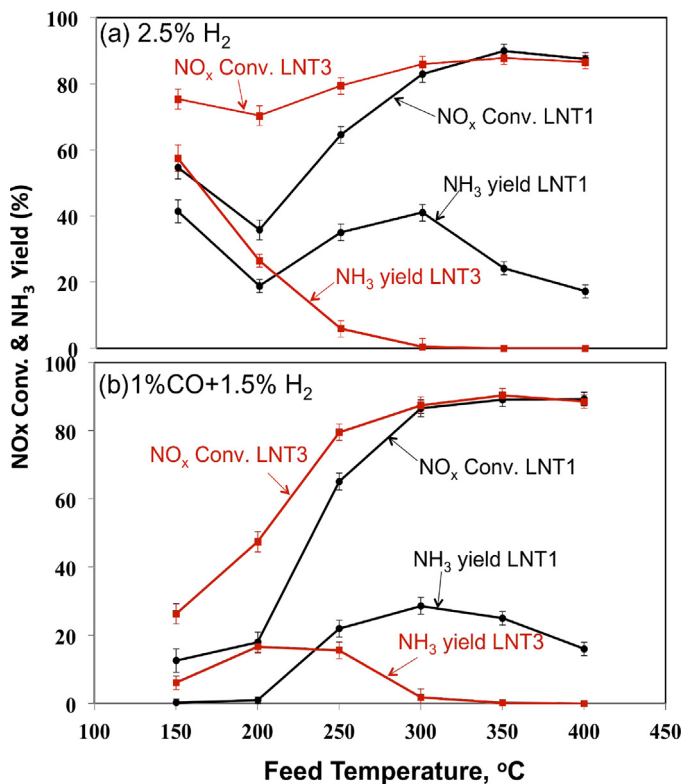

Fig. 1. Impact of ceria on NO$_x$ conversion and NH$_3$ yield from ceria-free LNT1 and ceria-rich LNT3 using (a) 2.5% H$_2$ and (b) 1% CO + 1.5% H$_2$ as reductants.

ceria. An added SCR top layer can minimize the downstream NH$_3$ consumption by effectively capturing released NH$_3$ for additional NO$_x$ reduction. Thus, ceria-rich LNT3 is more effective than ceria-free LNT1 in NH$_3$ generation and NO$_x$ adsorption for dual-layer application over the low temperature window (150–250 °C). For these reasons, LNT3 was chosen as the LNT layer in the dual-layer study.
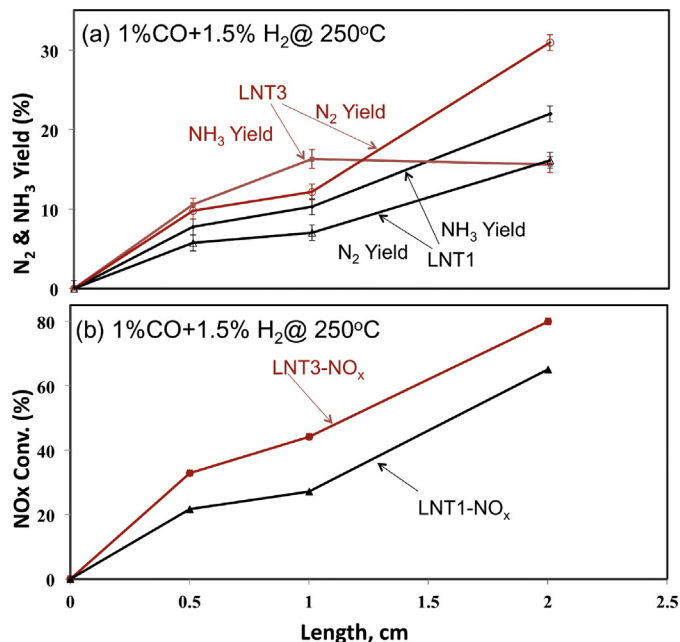

Fig. 2. Spatial NH$_3$, N$_2$ yields and NO$_x$ conversion along honeycomb catalysts of LNT1 and LNT3 with 1% CO + 1.5% H$_2$ as reductant at 250 °C.
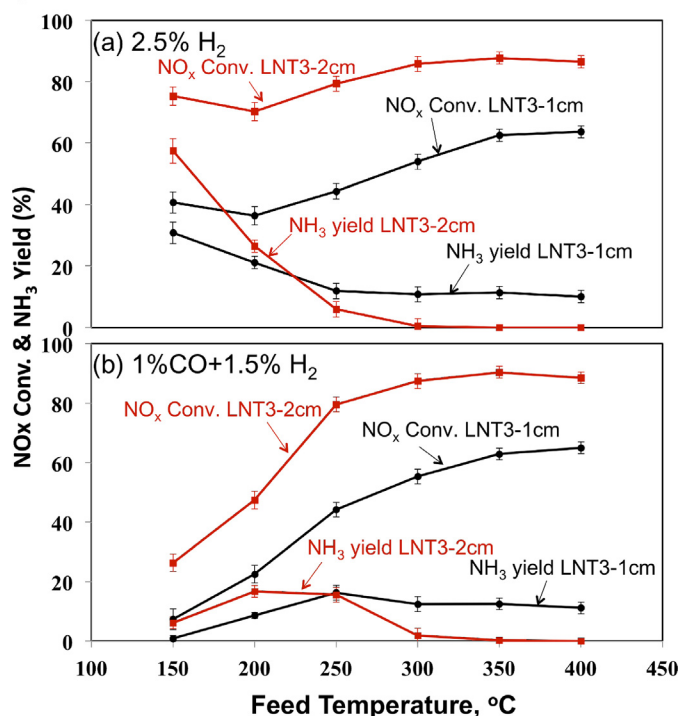
Fig. 3. NO_x conversion and NH_3 yield at the middle and the end of the LNT3 honeycomb catalyst using (a) 2.5% H_2 and (b) 1% CO + 1.5% H_2 as reductants.

Fig. 4. (a) NO_x, (b) NH_3 conversions for standard SCR reaction and (c) NH_3 storage capacity over CuZ, CuC, NaZ catalysts.

Fig. 3 compares the NO_x conversion and NH_3 yield at the middle point (1 cm) and the end (2 cm) of the LNT3. Below 250 °C, both upstream and downstream LNT3 zones have comparable deNO$_x$ contribution while the exit NH_3 yield is higher than that at the middle point. But at high temperatures (above 300 °C), the front half zone converts about 75% of the overall NO_x and almost the entire NH_3 yield under either pure H_2 or CO/H_2 feed. Almost no NH_3 is emitted at the downstream due to its oxidation by downstream stored NO_x and oxygen. In other words, the upstream LNT3 is the major NO_x reducer and NH_3 generator at high temperatures, which primarily determines the high-temperature performance. This finding will be referred to later.

3.2. Improved SCR catalyst for dual-layer application

The most suitable SCR catalyst for the dual-layer application should capture all the generated NH_3 at minimal loading (thickness) in order to minimize the diffusional resistance. To achieve high efficiency of trapped NH_3, the SCR layer activity should be high and minimally inhibited by the adsorbed NH_3, especially at low temperatures. Therefore, both high NH_3 storage capacity and low temperature SCR activity are highly desirable SCR attributes for the dual-layer application. Cu-ZSM-5 was used as the SCR catalyst in our previous dual-layer studies [9,21,22]. Peden et al. [28] reported that under the same reaction conditions for NH_3 SCR of NO_x, small pore Cu-SSZ-13 had superior activity and N_2 formation selectivity than larger pore Cu-Beta and Cu-ZSM-5 zeolites over the temperature range of 160–550 °C. In addition, Cu-CHA has much higher hydrothermal stability than Cu-ZSM-5, which is critically important for the real-word LNT–SCR application. In such applications, the SCR catalyst is inevitably exposed to high temperatures during the periodic desulfation of the LNT layer.

Fig. 4 compares the performance of CuZ, CuC and NaZ monolithic catalysts with the same loading in terms of standard SCR activity and NH_3 storage capacity. Fig. 4a and 4b show that both NO_x and NH_3 conversions of CuC catalyst are higher than those of
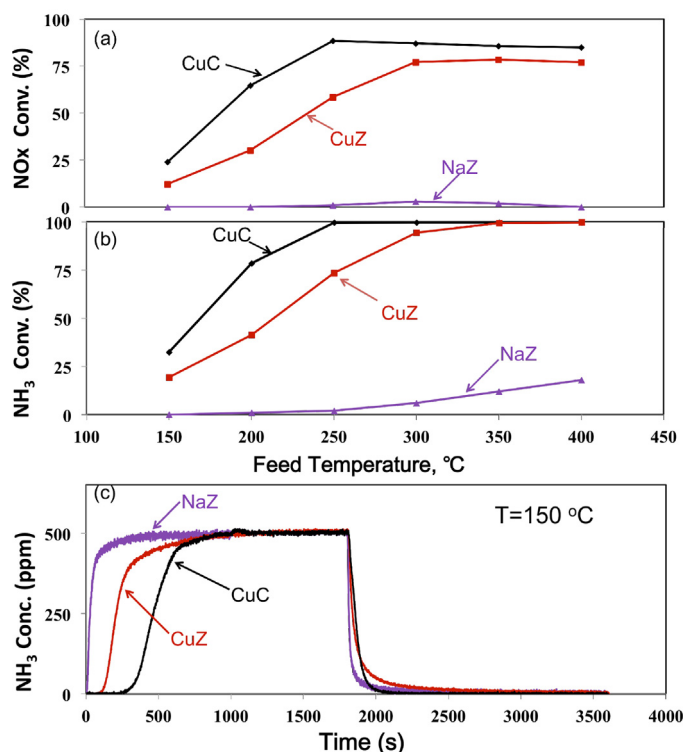
CuZ catalyst over the entire temperature range. These results are consistent with those of Peden [29]. Fig. 4c shows that the NH_3 adsorption capacity of the CuC catalyst is higher than that of the CuZ catalyst, i.e. more ammonia is chemisorbed on CuC than on CuZ. Note that NaZ exhibits significantly lower standard SCR activity and NH_3 storage capacity than either CuZ or CuC. Thus, it can serve as good inert material to check diffusion limitations, as discussed later. Hence, CuC is a better candidate for the SCR catalyst in dual-layer application.

Fig. 5 compares the performance of three catalysts, CuC(0.8)/L(4.6), CuZ(0.9)/L(4.6) and LNT3 only catalysts. The CuC layer leads to significantly higher low-temperature NO_x conversion than LNT3 only and CuZ/L catalysts due to more effective NH_3 adsorption and higher NH_3-SCR activity. Almost no NH_3 slip is detected from CuC/L over the entire temperature range for both rich feeds. Using pure H_2 as reductant, the NO_x conversion from the CuC/L decreases monotonically as the temperature increases. This can be attributed to decreased NH_3 yield and intensified adverse effects by the SCR layer as the temperature increases. As shown in Fig. 1a, the NH_3 yield drops dramatically from 57% at 150 °C to 6% at 250 °C. For CO/H_2 feed, NO_x conversion from CuC/L reaches a maximum at 250 °C and then decreases as the temperature rises. The increasing conversion to the left of the maxima is due to the decreased CO inhibition and increased NH_3-SCR activity, while the decreasing conversion to the right of the maxima is due to intensified diffusion limitation and lower NH_3 yield above 250 °C. In contrast, given the lower NH_3-SCR activity of CuZ, the LNT unit plays a larger role in the deNO$_x$ performance of CuZ/L. This results in a similar trend of NO_x conversion below 300 °C from either LNT3 or CuZ/L, which increases monotonically with temperature.

For both rich feed cases, CuC/L has the lowest NO_x conversion above 300 °C, probably due to higher washcoat diffusion resistance caused by the small-pore CHA structure. At high temperatures the effluent lean-phase NO_x slips from dual-layer catalysts are higher
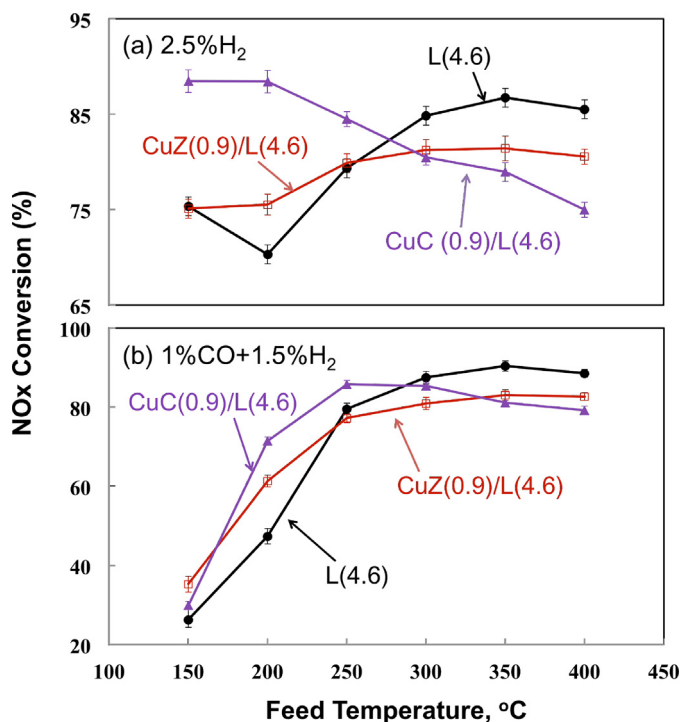
Fig. 5. Comparison of NO$_x$ conversion using (a) 2.5% H$_2$ and (b) 1% CO + 1.5% H$_2$ as reductants over L(4.6), CuZ(0.9)/L(4.6) and CuC(0.8)/L(4.6) catalysts.

Fig. 6. NO$_x$ conversion (a, b) and NH$_3$ yield (c) from dual-layer catalysts by 2.5% H$_2$ and GHSV = 120,000 h^{-1} at fixed LNT3 loading but different CuZ or NaZ loadings.

than that from LNT3-only catalyst, while lower NO$_x$ spikes are observed from dual-layer catalysts (data not shown). The decreased high-temperature NO$_x$ conversion from the dual-layer catalysts can be attributed to higher lean-phase NO$_x$ slip, likely due to the inhibited diffusion of NO$_x$ through the SCR layer. Peden et al. [29] reported that for the CHA SCR system, both washcoat and pore diffusion should be considered and effective diffusivities of the reaction gas molecules within the channel of SSZ-13 were lower than those in ZSM-5. These results demonstrate that CuC in dual-layer applications can maximize the low-temperature NO$_x$ conversion performance but compromise the high-temperature performance.

3.3. Impact of washcoat diffusion resistance from SCR top layer

Diffusion resistance due to the top SCR layer is arguably the most serious detriment for dual-layer application under high temperature and high flow rate. The thicker the SCR layer, the more severe is the washcoat diffusion limitation. However, a minimal thickness of SCR layer is required to guarantee the effective adsorption of NH$_3$. Thus, there is a trade-off between high NH$_3$ storage capacity and low diffusion limitation. In order to determine the optimal SCR loading for dual-layer application, it is necessary to know the effect of the diffusional resistance of the SCR top layer on the overall performance. Thus, a series of dual-layer CuZ/L catalysts with fixed LNT loading and increased SCR loading were prepared to study the impact of SCR loading. To intensify the diffusion limitations, the tests were carried out at high space velocity by shortening the length of the catalysts from 2 cm to 1 cm. The increase of space velocity decreases the contact time during which the gas species can diffuse through the SCR top layer to the LNT layer.

Fig. 6a shows the effect of increased SCR loading on the overall NO$_x$ conversion using 2.5% H$_2$ as reductant at 120,000 h^{-1} GHSV. It shows that the SCR top layer is beneficial for temperatures below 300 °C but somewhat detrimental above 300 °C. Increasing the SCR loading from 0.9 to 1.8 g/in.^{3} slightly increases the NO$_x$
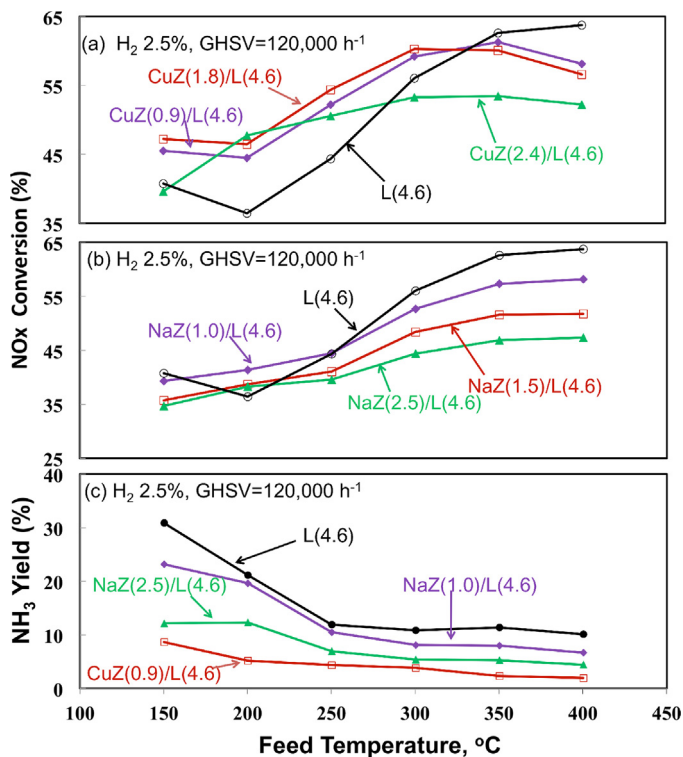
conversion below 300 °C. However, further increasing the SCR loading to 2.4 g/in.^{3} lowers the NO$_x$ conversion over the entire temperature range except at 200 °C. Above 300 °C, the NO$_x$ conversion decreased with increased SCR loading, indicating that the detrimental diffusion limitation of the SCR layer outweighs the benefit of additional NO$_x$ reduction. For example, at 400 °C the NO$_x$ conversion is 64% by the LNT3 catalyst alone. It is decreased to 58%, 56% and 52% for 0.9, 1.8 and 2.4 g/in.^{3} SCR layer loading, respectively. Hence, for CuZ/L dual-layer catalyst, CuZ loading on top of LNT3 loading of 4.6 g/in.^{3} should not exceed 1.8 g/in.^{3}. In other words, the corresponding LNT3/CuZ loading ratio should remain below ca. 2.5.

It is still unclear whether diffusion limitation or undesired NH$_3$ oxidation cause a larger loss of the high-temperature performance. It has not yet been determined to what extent and under what conditions the overall deNO$_x$ efficiency is affected by additional diffusion resistance in the SCR layer. Addressing these issues requires a decoupling of the impacts of the NH$_3$-SCR reaction and undesired NH$_3$ oxidation from that of the additional diffusion resistance on the overall NO$_x$ conversion. One approach is to replace the active CuZ layer by a top layer containing inert zeolite crystallites. This minimizes the interference from NH$_3$-SCR and NH$_3$ oxidation and focuses only on the diffusional resistance effect. We accomplished this by a Na-ZSM-5 layer with Si/Al ratio of up to 280 containing few Brønsted acid sites, to minimize NH$_3$ adsorption and SCR activity as shown in Fig. 4

A series of NaZ/L with fixed LNT loading and different NaZ loading was prepared and tested with different reductant mixtures at a GHSV of 120,000 h^{-1}. Fig. 6b shows that increasing the upper layer loading from 1.0 to 1.5 and 2.5 g/in.^{3} lowers the NO$_x$ conversion over the entire temperature range under pure H$_2$ feed. A similar trend is also observed under CO/H$_2$ feed, which is not shown here. The impact of additional diffusion resistance starts at 150 °C for pure H$_2$ feed and 200 °C for CO/H$_2$ feed when the top layer loading is 1.0 g/in.^{3} or higher. Compared to the LNT3-only catalyst, the

additional diffusion resistance starts to decrease the overall NO_x conversions of the three dual-layer catalysts at 250 °C. Fig. 6c compares the NH_3 yield from LNT3, CuZ(0.9)/L(4.6), NaZ(1.0)/L(4.6), NaZ(2.5)/L(4.6). NH_3 slip from two NaZ/L catalysts is higher than that from CuZ/L catalyst, which confirms that NaZ has minimal NH_3 adsorption and SCR activity. Increasing NaZ loading from 1.0 to 2.5 g/in.³ decreases the NH_3 yield over the entire temperature, likely due to increased diffusion resistance limiting the transport of NO_x and reductants to the underlying LNT layer for NO_x reduction and NH_3 generation. The performance loss due to top-layer diffusion resistance can be quantitatively determined. For example, at 350 °C for either pure H_2 or CO/H_2 feed, the loss of overall NO_x conversion due to diffusion resistance is approximately 5%, 10% and 15% for a top layer loading of 1.0, 1.5 and 2.5 g/in.³, respectively.

The above quantitative analysis of diffusion resistance allows us to determine whether additional diffusion resistance or undesired NH_3 oxidation plays a major role in the high-temperature performance loss. NH_3 yield from 1 cm LNT3 at 350 °C with H_2 reductant is about 10%, as shown in Fig. 3a. According to reports by Liu et al. [9] and Pihl et al. [12], the NO_x selectivity for NH_3 oxidation by O_2 increases with temperature to about 50% at 350 °C. Thus, even under an extreme case in which all the 10% NH_3 yield is completely oxidized on the precious metal sites by O_2 rather than NO, the corresponding NO_x yield is 5%. Considering that a fraction of stored NH_3 will react with NO_x in the SCR catalyst to produce N_2, the actual NO_x yield from NH_3 oxidation must be lower than 5%. This is lower than the diffusion resistance loss of 5% for 1.0 g/in.³ or 10% for 1.5 g/in.³ top-layer loading at 350 °C reported above. Hence, the additional diffusion resistance causes a larger loss to high-temperature performance than undesired NH_3 oxidation and needs to be minimized to get an optimum performance of the LNT–SCR dual-layer catalyst.

3.4. Impact of zoning SCR loading

SCR zoning is expected to minimize the adverse effects of SCR top layer while maintaining the improved low-temperature performance to strike a better balance between low- and high-temperature performance. Compared to a typical dual-layer architecture, consider a catalyst in which the first half has a LNT3 layer without SCR deposited on top, and SCR is deposited only on the second half of the LNT3 layer. This catalyst was prepared by linking a 1 cm $L(X_1)$ single-layer catalyst with a 1 cm $CuC(Y)/L(X_2)$ dual-layer catalyst to get the dual-zone dual-layer catalyst, named $L(X_1)+CuC(Y)/L(X_2)$ in Table 3. The "X_1" and "X_2" represents the LNT3 loading in the first and second half bottom layer, while "Y" denotes the downstream SCR top layer loading.

Fig. 7 compares the performance of three dual-layer catalysts having the same total LNT and CuZ loadings, but different CuZ loading profiles, i.e. upstream, downstream and uniform SCR loading. The downstream-SCR catalyst exhibits higher NO_x conversion than the other two catalysts over the entire temperature range for both reductant mixtures. The dual layer with upstream SCR loading has the lowest low-temperature performance as it is incapable of capturing NH_3 produced from the downstream LNT3. The one with uniform SCR loading has lowest high-temperature performance due to severe transport resistance and intensified NH_3 oxidation. Thus, a zoned dual-layer catalyst with a downstream SCR loading maximizes the low-temperature performance improvement and minimizes the loss to high-temperature performance.

We then applied SCR zoning to the dual-layer catalyst with CuC as the top SCR layer. Fig. 8 compares the performance of $L(4.6)+CuC(0.8)/L(4.6)$, $CuC(0.8)/L(4.6)$ and LNT3 only catalysts. The three catalysts have the same total PGM loading but the SCR loading of L+CuC/L is only half that of CuC/L in order to reduce diffusion resistance over the downstream of the LNT. The
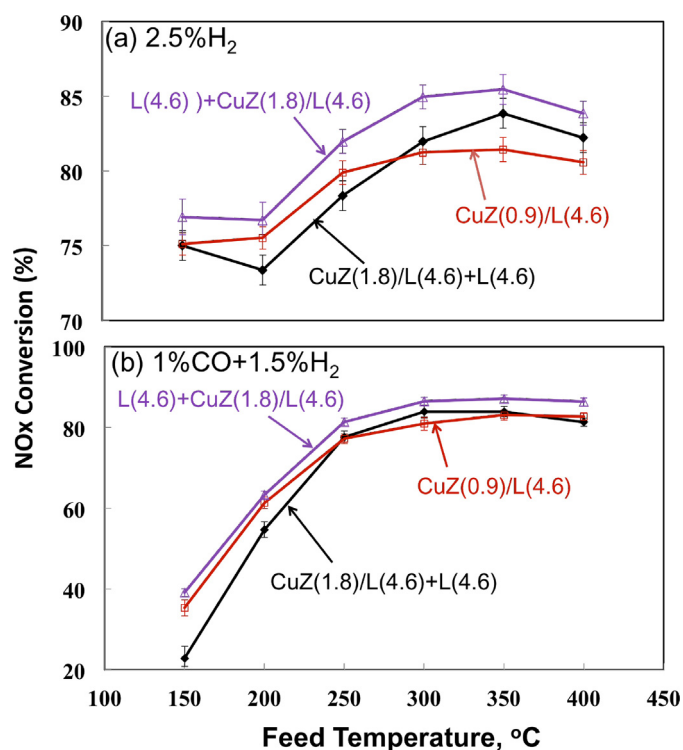
Fig. 7. Comparison of NO_x conversion by three dual-layer catalysts with the same total LNT and SCR loading but different SCR loading profiles using (a) 2.5% H_2 and (b) 1% $CO+1.5\%$ H_2.

dual-layer catalyst with downstream SCR loading has similar low-temperature NO_x conversion as the CuC/L, especially under CO/H_2 feed, and better high-temperature deNO$_x$ performance. Fig. 9 compares NO_x, NH_3 and N_2O effluent concentrations from the LNT3 and zoned dual-layer catalyst. It reveals that the effluent lean-phase NO_x slip from the zoned dual-layer catalyst is clearly lower than that from the LNT3, while only a slight decrease is observed in the
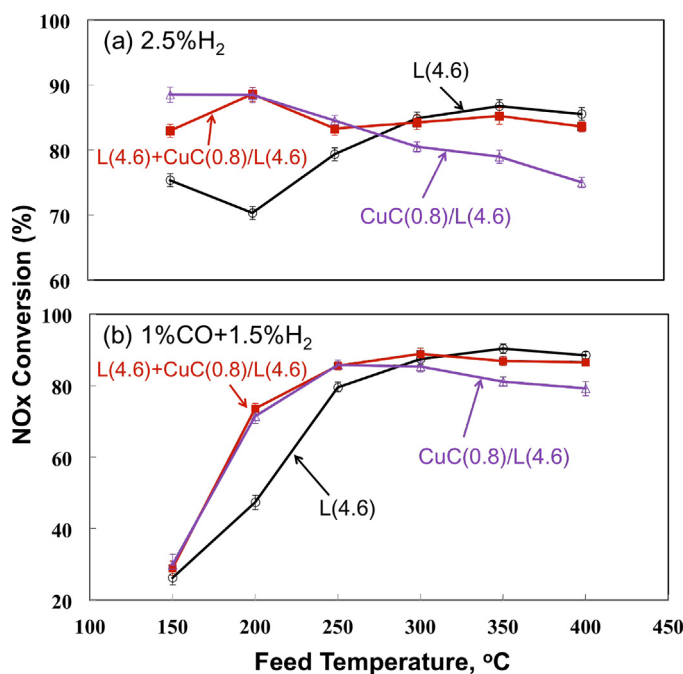
Fig. 8. NO_x conversion from LNT3, CuC(0.8)/L(4.6) and L(4.6)+CuC(0.8)/L(4.6) catalysts using as reductants (a) 2.5% H_2 and (b) 1% $CO+1.5\%$ H_2.
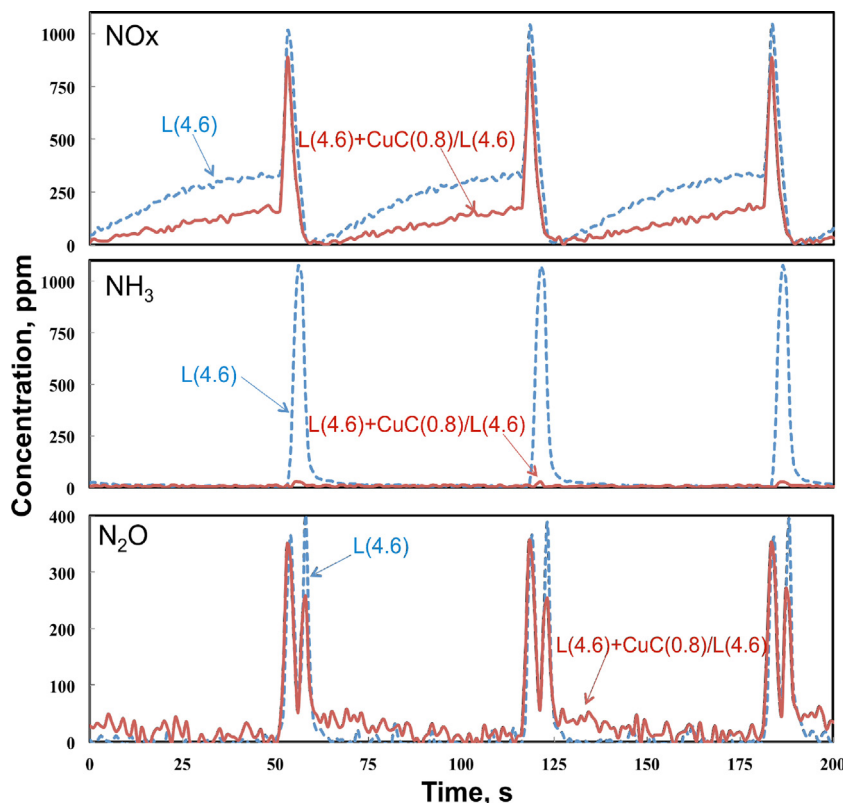
Fig. 9. Comparison of effluent concentrations of NO_x, NH_3, N_2O from L(4.6) and L(4.6) + CuC(0.8)/L(4.6) during cycling at 200 °C using 1% CO + 1.5% H_2 as reductants.

rich-phase NO_x puff. The added CuC layer with high NH_3 storage capacity captures almost all the NH_3. Thus, the incremental NO_x reduction by SCR layer mainly comes from the lean mode, where the NH_3 stored in the SCR layer can react with NO_x in the lean phase to reduce the NO_x slip. These results confirm that SCR zoning of dual-layer configuration can improve the low-temperature performance without compromising high-temperature performance. The CuC/L dual-layer catalyst with downstream SCR loading is the best dual-layer catalyst design of those examined.

Fig. 10 schematically illustrates the advantages of applying SCR zoning over conventional dual-layer architecture at high temperatures exceeding 300 °C. The downstream SCR layer enables the effective capture of NH_3 either from the upstream or underlying LNT catalyst for additional NO_x reduction, which improves the low-temperature performance. As mentioned above with respect to Fig. 3, the upstream LNT3 is the major NO_x reducer and NH_3 generator at high temperature, which primarily determines the high-temperature performance. Hence, the removal of upstream SCR layer minimizes the adverse impact of additional diffusion resistance on the overall NO_x conversion. Moreover, in conventional dual-layer catalysts most formed NH_3 is adsorbed by the SCR top layer at sites close to the LNT. The stored NH_3 proximal to LNT/SCR interface is likely to diffuse back to the adjacent LNT layer and be oxidized to NO_x at high temperatures during the lean phase. The zoned dual-layer catalyst can mitigate such undesired NH_3 oxidation by removing upstream SCR. The NH_3 released from the upstream LNT is then adsorbed by the top of the downstream SCR layer and then reacts with NO_x/O_2 to form mainly N_2,

N_2O formation from dual-layer catalysts exceeds that of LNT3 alone, especially under conditions favoring NH_3 generation, i.e. using pure H_2 at low temperatures. This is due to stored NH_3 oxidation by the adjacent LNT layer during the lean phase. Zoned dual-layer catalysts exhibit slightly lower N_2O slip than conventional dual-layer catalysts. For example, using 2.5% H_2 at 150 °C as

the reductant, a ∼16.2% selectivity to N_2O is measured over the LNT3 alone, while a ∼42.7% for the CuC(0.8)/L(4.6) and a ∼38.8% selectivity is obtained for the L(4.6) + CuC(0.8)/L(4.6). When adding CO to the rich feed and increasing the temperature, the N_2O emission from dual-layer catalysts drops and closes to that from the LNT-only catalyst.

3.5. PGM loading and zoning effect on dual-layer catalysts

A high PGM loading of the LNT catalyst is needed to meet the NO_x emission standards. This renders NSR technology too expensive for medium or heavy duty vehicles. According to a cost assessment of Tier 2 Bin-5 compliant $deNO_x$ aftertreatment systems by Posada et al. [30], the Cu-zeolite cost per liter of SCR brick is only about $2.40–$6, compared to the PGM cost of ca. $154 per liter of LNT brick based on precious metal price at that time. In other words, the LNT catalyst cost per liter is about 25–60 times that of Cu-zeolite. Another major concern lies in the dramatic volatility of the PGM prices, which may result in ever-changing catalyst costs during the product development cycle. During the past five years (2008–2013), monthly average platinum market prices have ranged from about $850 to $2000 with an average of ∼$1550 per troy ounce [31]. Upcoming stricter LEV III or Tier 3 emission regulations would require an increase of LNT catalyst volume, increasing further the catalyst cost. This makes LNT further less cost-effective compared to urea-SCR system. Therefore, it is crucial to reduce LNT catalyst loading while maintaining the performance.

Fig. 11a shows the performance when reducing LNT3 loading by half from 4.6 to 2.3 g/in.^{3} in a dual-layer catalyst. For a H_2 reductant, which is the best for NH_3 formation, the NO_x conversion of the dual-layer catalyst with half the LNT loading is slightly better than that of LNT3 only catalyst at 200 °C. This means that at least for a H_2 reductant, the dual-layer catalyst can reduce the LNT loading by half without degrading low-temperature $deNO_x$ performance. Fig. 11b
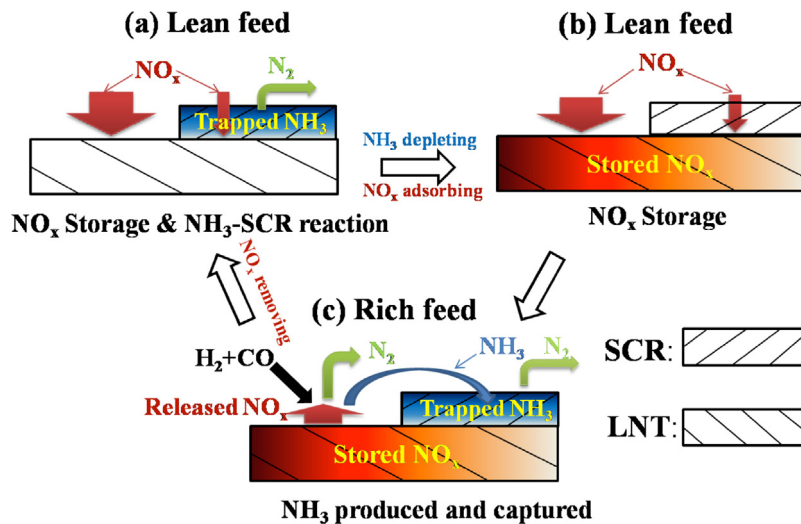
Fig. 10. Mechanism of NO_x decomposition by zoned dual-layer LNT–SCR catalyst at temperatures above 300 °C.

shows that for CO/H_2 feed, the NO_x conversions drops by 15–20% for the dual-layer catalyst relative to that of LNT3 catalyst over the entire temperature range. This occurs as NH_3 formation is inhibited by CO poison at low temperatures, restricting the beneficial impact of the SCR layer. Hence, reduction of the LNT loading in dual-layer catalysts is limited by the NH_3 yield at low temperatures.

Fig. 12 shows that compared to LNT3-only catalyst, reducing LNT3 loading of a dual-layer catalyst by 25% increases the low-temperature ($T < 300$ °C) NO_x conversion for pure H_2 feed and only slightly lowers for CO/H_2 feed. On the other hand, above 350 °C the NO_x conversions from these two dual-layer catalysts with different LNT loadings are similar but lower than that from LNT3 catalyst. This confirms that the reaction is diffusion limited at high temperatures. The SCR zoning can minimize the high-temperature loss.

Fig. 13 compares the NO_x conversion from LNT3 only, CuC(1.6)/L(3.45) and L(4.6) + CuC(1.6)/L(2.3). Both dual-layer catalysts have the same total LNT3 loading, which is lowered by 25% from that of LNT3 only catalyst. The SCR loading on the CuC/L is twice that of the L + CuC/L catalyst. Compared to the CuC/L catalyst, the L + CuC/L catalyst exhibits higher high-temperature NO_x conversion for both rich feeds, and also a better low-temperature performance for the CO/H_2 feed. The higher low-temperature conversion is due to LNT and SCR zoning. Higher upstream LNT loading, which is free of any top-layer diffusion resistance, makes the front zone an effective NO_x reducer and NH_3 generator over the entire temperature range. Compared with LNT3 only catalyst, L + CuC/L with less 25% LNT loading shows similar performance at high temperatures, but better performance at low temperatures under both
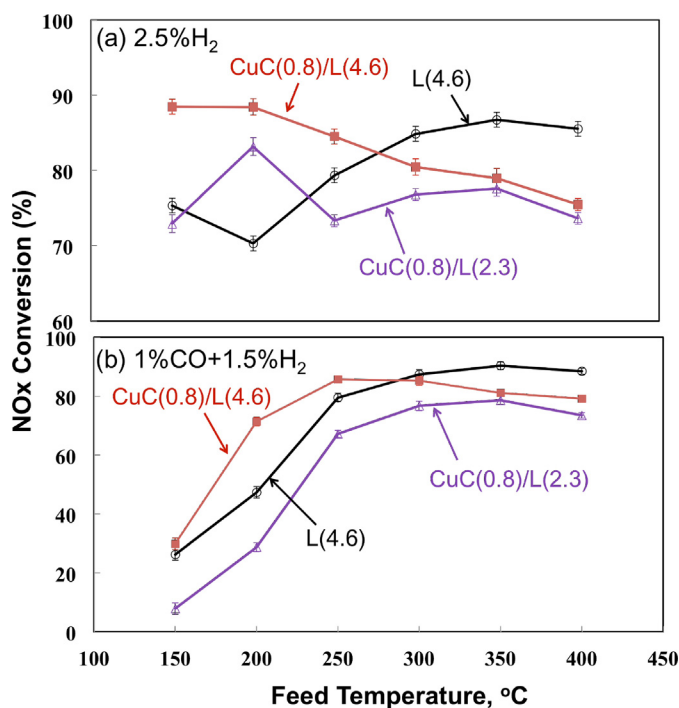

Fig. 11. NO_x conversion by LNT3 and two dual-layer catalysts having the same SCR loading but different LNT loadings by (a) 2.5% H_2 and (b) 1% CO + 1.5% H_2.
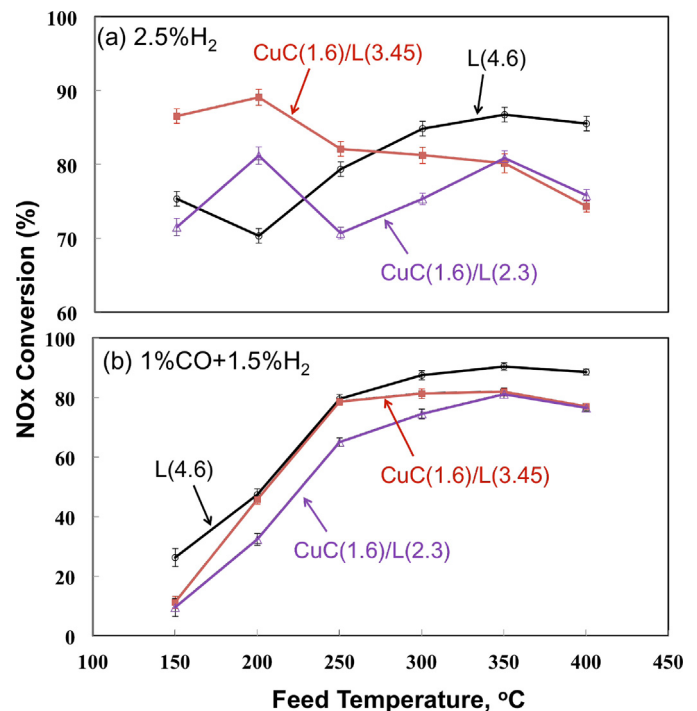

Fig. 12. NO_x conversion by LNT3 and two dual-layer catalysts having the same SCR loading but different LNT loadings using as reductants (a) 2.5% H_2 and (b) 1% CO + 1.5% H_2.
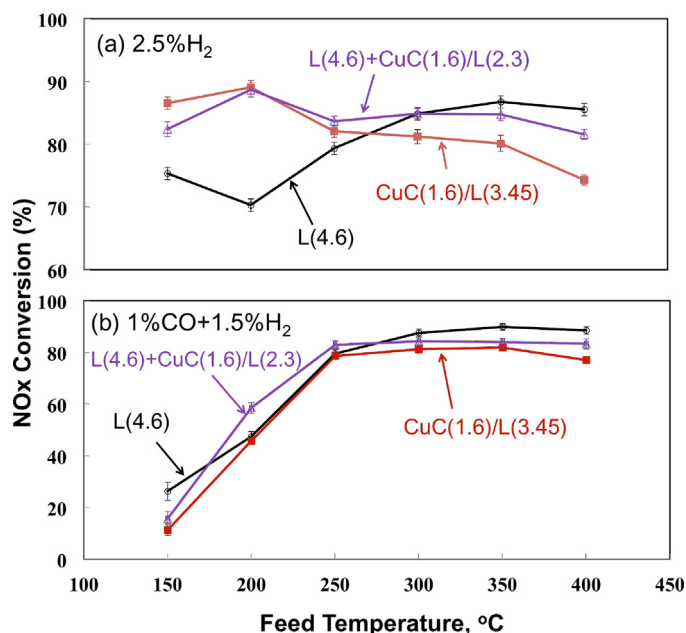
Fig. 13. NO$_x$ conversion by dual-layer catalysts with different zoned LNT and SCR loadings but the same total LNT loading using (a) 2.5% H$_2$ and (b) 1% CO + 1.5% H$_2$.

feeds except for 150 °C with CO. Thus, SCR and LNT zoning in dual-layer catalyst improves the deNO$_x$ performance relative to normal dual-layer catalyst over the entire temperature range. This enables better compensation for activity loss by decreased LNT loading.

Fig. 14 compares the NO$_x$ conversion of three zoned dual-layer catalysts with different downstream LNT loadings. Compared to L(4.6), the LNT3 loading is reduced by 12.5%, 25% and 37.5% for L(4.6)+CuC(1.6)/L(3.45), L(4.6)+CuC(1.6)/L(2.3) and L(4.6)+CuC(1.6)/L(1.15), respectively. Higher downstream LNT loading increases low- and high-temperature NO$_x$ conversion. Zoned dual-layer catalyst with 37.5% lower LNT loading still has
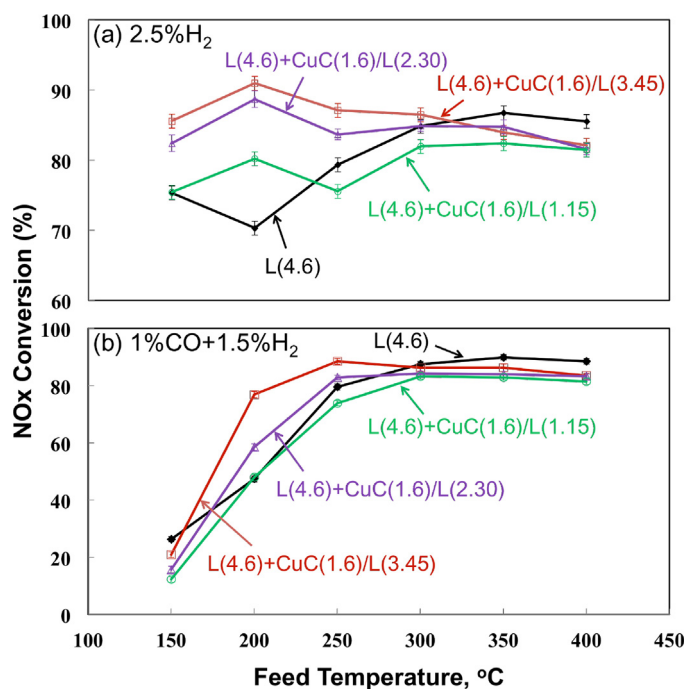

Fig. 14. NO$_x$ conversion by dual-zone dual-layer catalysts with different downstream LNT loadings using (a) 2.5% H$_2$ and (b) 1% CO + 1.5% H$_2$.

a comparable deNO$_x$ efficiency to L(4.6), ∼5% lower in average, over the entire temperature range for both rich feeds. Note that the commercial LNT3 catalyst used in our study is not optimized for dual-layer application. It is desirable to reduce the expensive PGM loading at constant barium and ceria loading to maintain the NO$_x$ storage capacity, rather than decreasing total LNT loading.

The lean/rich duration is fixed to 60 s/5 s during our study. The optimization of lean/rich cycling timing and rich regeneration control is expected to attain better deNO$_x$ performance. Thus, it would be more helpful to explore the minimum feasible PGM loading based on the optimized LNT catalyst and operating conditions. This preliminary study demonstrates that the zoned LNT–SCR dual-layer catalyst has the potential to reduce PGM loading up to 37.5% under the laboratory test conditions used in this study. This will enable the LNT-based system more cost competitive with the urea-SCR system for application in passenger cars.

4. Concluding remarks

The zoned LNT–SCR dual-layer catalyst has the potential to reduce PGM loading without compromising overall deNO$_x$ efficiency. The main findings are:

- High ceria level (34 wt%) in LNT improves the low-temperature performance of the dual-layer catalysts, due to enhanced NO$_x$ adsorption and NH$_3$ generation at low temperatures (150–250 °C). And using CuC instead of CuZ as SCR layer further enhances the low temperature performance of the dual-layer catalyst
- Depositing an inert Na-ZSM-5 with a high Si/Al ratio of 280 instead of the active Cu-zeolite layer allows decoupling the impact of the NH$_3$-SCR reaction and NH$_3$ oxidation from that of the additional diffusion resistance on NO$_x$ conversion. A zeolite top-layer of 1.0 g/in.^{3} causes diffusion limitation at temperatures exceeding 150 °C for pure H$_2$ feed and 250 °C for CO/H$_2$ feed at a GHSV of 120,000 h^{-1}. In addition, washcoat diffusion limitation adversely affects high temperature performance more than does NH$_3$ oxidation to NO$_x$.
- Zoned dual-layer catalyst with downstream SCR loading can maintain the enhanced deNO$_x$ efficiency at low temperature, while minimizing the high-temperature performance loss caused by the additional diffusion resistance and undesired NH$_3$ oxidation.
- Zoning of both SCR and LNT in dual-layer catalyst increases the deNO$_x$ performance over that of a conventional dual-layer catalyst over the entire temperature range. This enables a large reduction of the PGM loading.
- The zoned dual-layer catalyst exhibits a potential PGM loading reduction of up to 37.5% with comparable deNO$_x$ performance to that of LNT3 only catalyst.

Finally, the operating conditions adopted by this study favor NH$_3$ generation and NH$_3$ is the sole reductant for the incremental NO$_x$ reduction in the SCR of the dual-layer catalysts as the rich reductants was a CO/H$_2$ mixture. HC and relatively high CO concentration in engine exhaust may affect some of the conclusions. A detailed study on dual-layer catalysts under simulated exhaust condition will be reported elsewhere [32].

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